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OBSERVATIONS AND NOTES ON THE EFFECT OF METHANOL ANTIFREEZE ON HEALTH[1]

By R. R. Sayers[2] and W. P. Yant[3]

The rather sudden increase in the use of methanol as an antifreeze for automobile radiators has caused considerable comment, with some anxiety to persons interested in industrial and public health, regarding the possible health hazard in dispensing and using the product. In view of this, the chemical industry interested in the manufacture and marketing of methanol requested the Bureau of Mines to make an impartial and extensive investigation of the hazard involved. With the assistance of the industry this investigation is now in progress and will extend throughout the present winter. When these observations are finished a complete report will be made. At present, however, the acute interest in the problem and the many inquiries that have been received from manufacturers of methanol, garage owners, the automotive industry, public health officials, and private persons demands a brief statement relative to the reasons for the recent availability of methanol for antifreeze purposes, the plan of the bureau's investigation, and the trend of the results of the investigation obtained to date.

REASONS FOR AVAILABILITY OF METHANOL ANTIFREEZE

Methanol is neither a new nor an uncommon chemical compound. It has been marketed under many different chemical and trade names, some of which are methyl alcohol, wood alcohol, wood spirit, methyl hydrate, wood naphtha, Columbia Spirits and Colonial Spirits. Millions of gallons have been used by millions of people during the past 30 years, principally for solvent purposes, for the manufacture of formaldehyde, and for denaturing ethyl alcohol. It has not been marketed heretofore to a large extent for antifreeze purposes, principally for the reason that, since the advent of extensive use of automobiles, the cost of methanol has exceeded that of denatured ethyl alcohol. Recently methanol has become available in large quantities and at a markedly lower cost than heretofore. This has not been due to expansion or development in the wood distillation industry, but entirely to the development of a synthetic process for making the product. The new process was originally conceived and developed in France and Germany, primarily from the viewpoint of increasing uses of coal and gas and with the particular viewpoint of the developments of future liquid motor fuels.

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1 - The Bureau of Mines will welcome reprinting of this paper, provided that the following footnote acknowledgment is used: "This report represents work done under a cooperative agreement between the U. S. Bureau of Mines and the Carbide & Carbon Chemicals Corporation, DuPont Ammonia Co., and the Commercial Solvents Corporation. Reprinted from U. S. Bureau of Mines Information Circular 6415."

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The process has readily found adoption in the United States for the utilization of heretofore waste gases and in the manufacture of industrial chemicals. As a result the cost of methanol has been markedly reduced during the past two years and, as stated previously, can be produced at a cost which places it in competition with denatured alcohol for use as an antifreeze.

PREVIOUS USE OF ANTIFREEZE METHANOL

The use of methanol as an antifreeze for automobile radiators is not entirely a recent innovation. The product, both crude and refined, has been used for many years in radiators in communities where wood distillation plants are located. More recently, particularly the winter of 1929-30, it has gained in general usage; and for the present winter, 1930-31, it is estimated that from 10 to 15 per cent of the low-boiling antifreeze materials used will be methanol. The product is at present dispensed to the consumer as a mixture of 76.5 per cent methanol and 23.5 per cent water. It has been found that 1 gallon of this mixture of methanol and water has an antifreeze value equivalent to that of 1 gallon of antifreeze ethyl alcohol.

TOXICITY OF METHANOL

The observations and discussions of the poisonous effect of methanol which have been recorded in the literature are in many cases conflicting and confusing. Some have explained the differences in results on the basis of individual susceptibility. While this explanation is no doubt valid in part it is also just as possible that many of the differences arise through the difficulty in obtaining accurate quantitative details, particularly if it involves the possible use of methanol for beverage purposes. In surveying past experience, however, there are certain consistent observations.

It has been shown beyond doubt that methanol is a poison and will produce serious poisoning when sufficient amounts are taken into the body. Also there is no practical difference between the toxicity of crude and refined methanol or between methanol made by the wood distillation process and that made by the recent synthetic process. Further, it can not be made nonpoisonous by any known method or process. These facts need emphasis because some persons have held the erroneous opinion that the poisonous action of methanol is due mainly to impurities and that the purified product is relatively less toxic.

The quantity of methanol required to produce poisoning when the product is taken into the stomach is pretty well known. Small amounts have been taken without apparent harm, but on the average 1 to 2 ounces (the contents of one to two ordinary whiskey glasses) will cause serious poisoning with possibly blindness and death, and twice that amount will frequently cause death.

The effects of inhaling air containing various amounts of methanol vapor are not so well known. Wide experience over many years has shown that there are conditions of exposure to methanol vapor in the air which cause no apparent harm, and also that there are conditions which will produce serious poisoning. Records of cases of severe poisoning by inhaling methanol vapor, however, show the large majority of serious cases to have occurred in the use of methanol, principally as a solvent for paints and varnishes, in relatively small confined and unventilated places. The use of shellac dissolved in methanol for coating the interior of beer vats has been an important source of trouble of this kind. The potential health hazards from air containing methanol vapor thus depend on the degree of exposure; accordingly the safety of methanol for antifreeze purposes depends on whether or not the exposure involved in a particular usage will exceed the range of tolerable exposure.

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Less is known of the dangers to health from absorption of methanol through the skin. In reviewing the literature no conclusive information could be found that serious poisoning has been acquired in this manner. A few cases are described as possibly being due to skin absorption. In these cases the exposure was either so slight that it is rather hard to believe that the trouble was due to absorption of methanol through the skin, or the situation was complicated by the possibility of high concentrations of vapor in the air breathed. When one considers the large amounts of methanol that have been used and the frequency with which it has undoubtedly come in contact with the skin, in many instances even having been used for treatment of wounds and for "rubbing" purposes, it is apparent that no appreciable hazard exists from this manner of exposure to methanol as an antifreeze.

SCOPE OF BUREAU OF MINES INVESTIGATION

The primary objective of the investigation being conducted at present by the Bureau of Mines is to ascertain whether or not the use of methanol for antifreeze purposes will constitute a health hazard to persons involved in its distribution and use. In more detail, the investigation entails a laboratory study of the toxicity of methanol when acquired by inhaling air containing its vapor and when acquired by skin absorption. Simultaneously with the laboratory study, a practical field investigation is being made of the amount of methanol vapor to which persons are exposed in closed cars and in private and public garages due to escape of the vapor from the radiator, or spillage and drip from leaky radiators. The exposure of the garage or filling station attendant while dispensing methanol is also considered. The conditions under which the tests are being made range from the normal operating conditions to overheated engines and boiling radiators.

In addition to the field investigation pertaining to the conditions encountered in the use of methanol as an antifreeze, an investigation is being made of the exposure and the health experience in the manufacture of methanol. This phase of the investigation affords opportunity for obtaining information based on long experience with methanol under many conditions of exposure which simulate those encountered in its use as an antifreeze, and thereby gives earlier information on continued exposure than is possible to obtain from a study of antifreeze usage.

The study made by the Bureau of Mines will not include work on the toxicity of methanol when taken into the stomach. It is not only a well-known fact that it will produce serious poisoning, but the quantities required to produce poisoning have been established. Further, the ingestion of enough methanol to cause poisoning is not an apparent hazard in its use as an antifreeze.

RESULTS OF BUREAU OF MINES INVESTIGATION

Although the Bureau of Mines investigation will not be completed for several months, the results to date have yielded certain information which is pertinent in evaluating the possible hazards from the use of methanol as an antifreeze. A survey of the conditions of exposure prevailing in four plants engaged in the manufacture of methanol, and physical examination of 36 men who have worked in these plants for periods of a few months to 10 to 15 years, has been completed. This survey consisted of making general observations of duties and exposure of the workmen, quantitative chemical determinations of the amount of methanol to which the workmen were exposed, and a physical examination of the workmen. The physical examination included an occupational history, a health history, and a complete physical examination with special attention to vision, pupil reflex, and eye pathology as revealed by

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ophthalmoscopic examination. Urine specimens were examined for albumen, sugar, specific gravity, reaction to litmus, and methanol content; and blood specimens for methanol, hemoglobin content, number of red and white cells, and differential cell counts.

These persons were engaged in all the operations of manufacturing methanol wherein there was exposure to air containing the vapor and exposure by contact with the skin. In nearly all cases both types of exposure were present. The manner of exposure to vapor ranged from working over drums being filled with methanol, inserting bungs in filled drums the exterior of which was usually wet with drippings, working over an open drain pan continuously wet with methanol, taking samples of methanol from drums and still-house lock-boxes, making hydrometer tests, and general exposure resulting from leaks and spillage in the working places.

Contact with the skin was a common finding, occurring many times daily with some persons. In one operation a man wet the palm and fingers of one hand two hundred to three hundred times daily and in addition to this was continuously working over drums being filled with antifreeze methanol. In a similar operation another person wore gloves, the palms and fingers of which were wet almost constantly. Other operations required almost constant contact of the fingers with methanol. It is a rather common practice among still-house operators at wood distillation plants to wet their hands with methanol and smell the product as a guide in still operation. Likewise it is a common practice at these plants to use methanol for washing wood tar from the hands and tools and for cleaning parts of machinery.

The above are usual and observed exposures. Under unusual conditions it was learned by interview of workmen that some frequently get their trouser legs wet, and others on a number of occasions have been practically drenched with methanol. They stated that the usual procedure in these cases is to merely allow the methanol to evaporate as they suffer no discomfort other than the cooling effect produced by the rapid evaporation. A number of persons stated that they had used methanol on wounds, and as a liniment for "rubbing" purposes, and a considerable number had used it in automobile radiators for antifreeze.

None of the men expressed fear of exposure to the vapors or by skin contact for the reason that they had never experienced ill-health from it nor did they know of serious effects having occurred to workers in the industry from this manner of exposure. There is, on the other hand, universal knowledge that methanol is poisonous and can not be taken into the stomach.

The results of the physical examination of these men revealed no acute or chronic illness and no defective vision or eye pathology attributable to methanol. There was also no indication of deleterious action revealed by blood and urine analysis. In a considerable number of cases of comparatively severe exposure, methanol was found in both the blood and urine when the specimens were taken after several hours' work. This confirms actual exposure and acquiring methanol but, on the other hand, substantiates experience that certain amounts of methanol can be acquired without apparent harm. Specimens taken the following morning from several of these persons showed methanol to be practically absent in most cases and markedly reduced in the others. In all cases the amounts in the blood and urine were far below those which have been found in the laboratory part of the study to be harmful to dogs.

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SUMMARY

The information which the Bureau of Mines has obtained to date indicates that there is no hazard to health from the reasonable use of methanol for antifreeze purposes. Many of the conditions of exposure to vapor and by contact with the skin, which were observed in the manufacture of methanol and for which no health hazard was found, are very comparable to the degree of exposure observed in usage as an antifreeze. Also the exposure in both cases is below those which laboratory experiments with animals have indicated to be harmful.

The investigation is being continued for the completion of information on the toxicity of methanol, particularly from the viewpoint of obtaining more comprehensive data regarding allowable concentrations for industrial uses and for investigating further the mechanism of methanol poisoning. Also, while there are no reasons to believe danger to health will occur in the use of the product as an antifreeze, the Bureau of Mines will observe its use throughout the present winter, as this procedure is always desirable where new uses of products involve the question of hazard to health.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are based on studies and observations to date.

1. Observations made by the Bureau of Mines have indicated that there is no danger of poisoning from the reasonable use of methanol as an antifreeze for automobile radiators.

2. The evidence that methanol poisoning has been caused by absorption through the skin is rare and inconclusive.

3. Practically continuous exposure to low concentrations and short intermittent exposure to high concentrations of methanol cause no apparent harm; but, on the other hand, continued exposure to high concentrations will cause serious poisoning.

4. All methanol, whether made by wood distillation methods or synthetic methods, or whether it is crude, refined, or highly purified, is poisonous when taken internally. It will cause serious poisoning, blindness, and possibly death when as little as 2 ounces is taken into the stomach.

5. To avoid misuse it is recommended that in the future all antifreeze methanol be brightly colored to enable garage attendants and the public to identify it as methanol; and to warn against misuse, particularly for beverage purposes.

6. The largest producers of methanol antifreeze label their containers so as to call attention to the hazards of misuse of methanol and also issue information and instructions to garage attendants and the consuming public warning against its misuse. It is recommended that these precautionary measures be adopted by all producers.

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